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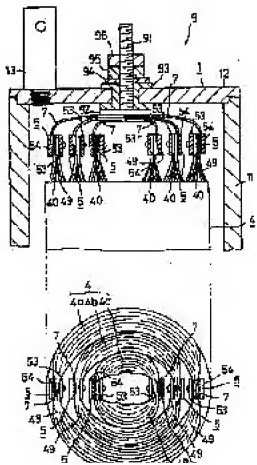
(54) CYLINDRICAL NONAQUEOUS ELECTROLYTIC SOLUTION SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a cylindrical nonaqueous electrolytic solution secondary battery having lower internal resistance and better productivity than a conventional battery.
SOLUTION: In the cylindrical nonaqueous electrolytic solution secondary battery, a non-coated section which is a part of a core comprising a positive or negative electrode and is not coated by an active material, protrudes at an end of a winding electrode body 4 in the direction of an axis. A plurality of collector electrodes 5 are mounted on a protruding section. Each collector electrode 5 comprises a rivet 54 and a washer 53. The rivet 54 has a tabular head and a shaft. The shaft penetrates a non-coated core bundle 49, a reed 7 and the washer 53. An end of the shaft is narrowed. The non-coated core bundle 49 and the reed 7 are pressed between the tabular head and the washer 53. Each reed 7 is coupled to an electrode terminal 9.



NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]The rolling-up electrode body used as a rechargeable battery element is accommodated in the inside of a battery can, and this invention relates to the cylindrical nonaqueous electrolyte secondary battery which can roll round from the electrode terminal part of the couple provided in the battery can, and can take out the generating electric power of an electrode body.
[0002]
[Description of the Prior Art]In recent years, the rechargeable lithium-ion battery with a high energy density attracts attention as a power supply of a portable electronic apparatus, an electromobile, etc. For example, as shown in drawing 4 and drawing 5, inside the cylindrical battery can (1) which carries out welding immobilization of the lid (12) and (12), the comparatively big cylindrical rechargeable lithium-ion battery of capacity used for an electromobile accommodates the rolling-up electrode body (2) shown in drawing 6 in the both ends of a barrel (11), and is constituted to them. The electrode terminal mechanism (9) and (9) of the positive/negative couple is attached to both the lids (12) and (12).
It is possible for two or more the two poles and the two-electrodes terminal mechanisms (9) and (9) of a rolling-up electrode body (2) to be mutually connected by the electrode tab (3) of a book, respectively, and to take out outside the electric power which a rolling-up electrode body (2) generates from the electrode terminal mechanism (9) of a couple and (9).
The gas exhaust valve (13) of the pressure sliding type is attached to each lid (12).
[0003]The rolling-up electrode body (2) shown in drawing 6 makes a band-like separator (22) intervene between a band-like anode (21) and negative electrode (23), respectively, winds these spirally and is constituted. An anode (21) applies the positive active material (24) which consists of a lithium multiple oxide to both sides of the band-like axis which consists of aluminium foil, and is constituted, and a negative electrode (23) applies the negative electrode active material (25) containing a carbon material to both sides of the band-like axis which consists of copper foil, and is constituted. Nonaqueous electrolyte is impregnated with the separator (22). The base end of two or more electrode tabs (3) was joined to the anode (21) and the negative electrode (23) by spot welding etc., respectively, and the tip part is projected from the rolling-up electrode body (2). The electrode tab (3) joined to the anode (21) is formed from aluminium foil, and the electrode tab (3) joined to the negative electrode (23) is formed from copper foil.

[0004]And as shown in drawing 5, the tip part (31) of two or more electrode tabs (3) with same polarity is connected to one electrode terminal mechanism (9). In drawing 5, only the state where the tip part of some electrode tabs is connected to the electrode terminal mechanism (9) is shown for convenience, and the graphic display in the state where the tip part is connected to the electrode terminal mechanism (9) is omitted about other electrode tabs.

[0005]An electrode terminal mechanism (9) is provided with the electrode terminal (91) attached by penetrating the lid (12) of a battery can (1), and the flange (92) is formed in the base end of this electrode terminal (91). The breakthrough of a lid (12) is equipped with an insulating member (93), and the electrical insulation and sealing nature between a lid (12) and an electrode terminal (91) are maintained. A washer (94) is inserted in from the outside of a lid (12), and the 1st nut (95) and the 2nd nut (96) are screwing in an electrode terminal (91). And sealing nature is improved by binding the 1st nut (95) tight and compressing an insulating member (93) with the flange (92) and washer (94) of an electrode terminal (91). The tip part (31) of said two or more electrode tabs (3) is being fixed to the flange (92) of an electrode terminal (91) by spot welding or ultrasonic welding.

[0006]By the way, in a rechargeable lithium-ion battery, since the length of an anode and a negative electrode becomes large with enlargement of a cell, in the collecting structure by the electrode tab like ****, the problem of current collection nature being low, and dispersion occurring in internal resistance, or service capacity falling arises.

[0007]Then, the **** collecting structure shown in drawing 7 is proposed in order to cover the overall length of an anode and a negative electrode and to obtain uniform current collection nature. The anode (41) in which a rolling-up electrode body (4) applies positive active material (44) on the surface of an axis (45) similarly in this collecting structure, Although it comprises a negative electrode (43) which applies negative electrode active material (46) on the surface of an axis (47), and a separator (42) with which nonaqueous electrolyte was impregnated, respectively an anode (41) and a negative electrode (43) are shifted crosswise, are piled up on a separator (42), and are rolled round spirally. By this, at one end, among the both ends of the volume shaft orientations of a rolling-up electrode body (4). The edge (48) of the axis (45) of an anode (41) projects to the method of outside [edge / of a separator (42)], and the edge (48) of the axis (47) of a negative electrode (43) has projected to the method of outside [edge / of a separator (42)] in the end of another side. And in the both ends of a rolling-up electrode body (4), a disc-like collecting electrode plate (32) is welded with the edge (48) and (48) of the axis of positive/negative two poles, respectively, and this collecting electrode plate (32) is connected to said electrode terminal mechanism (9) via a lead member (33).

[0008]However, in the nonaqueous electrolyte secondary battery which has the collecting structure shown in drawing 7, Since the area of the edge (48) of the axis (45) which constitutes the anode (41) and negative electrode (43) of a rolling-up electrode body (4), and (47), and (48) was small, the touch area between the axis edge and a collecting electrode plate (32) was small, and there was a problem to which the internal resistance of a cell becomes large by this. In order to obtain high power, it is required to reduce internal resistance as much as possible, and the collecting structure excellent in productivity is needed further for manufacturing-cost reduction.

[0009]In then, the state where rolled round this collecting electrode plate (62) and it pushed against the axis edge (48) of an electrode body (4) using the collecting electrode plate (62) which formed two or more bend parts (64) in the plate-like main part (63) as shown in drawing 8. The collecting structure which welds this bend part (64) by resistance to the axis edge (48) is proposed (for example, refer to

JP,11-31497,A).

[0010]Replace with a disc-like collecting electrode plate, roll round the collecting member (65) in which two or more slits (66) were cut as shown in drawing 9, and it installs in the end of an electrode body (4), In the state where the axis edge (48) was made to insert in the slit (66) of this collecting member (65), it irradiates with a laser beam on the surface of a collecting member (65), and the collecting structure which performs laser welding is proposed (for example, refer to JP,10-261441,A).

[0011]

[Problem(s) to be Solved by the Invention]However, in the collecting structure which welds by resistance the collecting electrode plate which formed the bend part like drawing 8, when the thickness of an axis was very small like a rechargeable lithium-ion battery, not only welding is difficult, but there was a problem that the electrical resistance in a weld zone was large, and collecting performance was still low.

[0012]The collecting member which has complicated shape is not only needed, but in the collecting structure which carries out laser welding of the collecting member in which two or more slits were cut like drawing 9 to the axis edge, since the welding operation to a collecting member was required, there was a problem inferior to productivity.

[0013]The purpose of this invention has internal resistance lower than before, and is providing the cylindrical nonaqueous electrolyte secondary battery which has the collecting structure which excelled [**] in productivity.

[0014]

[Means for Solving the Problem]In a cylindrical nonaqueous electrolyte secondary battery concerning this invention, A rolling-up electrode body (4) which made a separator (42) containing nonaqueous electrolyte intervene between a band-like anode (41) and a negative electrode (43), respectively, and rolled these round spirally inside a battery can (1) is stored, An anode (41) and a negative electrode (43) apply an active material to the surface of a band-like axis, are constituted, and can take out electric power which a rolling-up electrode body (4) generates from an electrode terminal part of a couple to the exterior, respectively. At at least one end of volume shaft orientations of this rolling-up electrode body (4). An axis non-coating part (40) by which an active material is not applied to an axis which constitutes an anode (41) or a negative electrode (43) projects, This lobe is divided into two or more ring shape fields (4a) (4b) (4c), Each ring shape field is governed by non-coating axis bunch (49) with collecting terminals (5) at 1 of the hoop direction, or two or more places, Each collecting terminals (5) comprise a rivet member (54) and a washer member (53) which have been arranged on both sides of a non-coating axis bunch (49) at both sides, and a rivet member (54) has a plate-like head (51) and a shank (52). And a shank (52) penetrates a non-coating axis bunch (49), a lead (7), and a washer member (53), By closing a tip part of this shank (52), a non-coating axis bunch (49) and a lead (7) are compressed between a plate-like head (51) of a rivet member (54), and a washer member (53), and each lead (7) is connected with an electrode terminal part.

[0015]In composition of a cylindrical nonaqueous electrolyte secondary battery of above-mentioned this invention, each collecting terminals (5) have a simple structure which comprises a rivet member (54) and a washer member (53). Since each collecting terminals (5) are attached to each non-coating axis bunch (49) of a rolling-up electrode body (4) by caulking immobilization, they do not need to perform welding etc. and are as simple as a fitter. A non-coating axis bunch (49) is strongly compressed by a plate-like head (51) and a washer member (53) of a rivet member (54) from both sides, and axis sides

are stuck by pressure strongly, and. Since a shank (52) of a rivet member (54) has penetrated a non-coating axis bunch (49) and a lead (7), even if big pull strength acts on collecting terminals (5), there is no possibility of separating from a non-coating axis bunch (49) and a lead (7). Thus, the axis sides of a non-coating axis bunch (49) are stuck by pressure strongly mutually, and a non-coating axis bunch (49) and a lead (7), Since it is being strongly stuck by pressure with an inner surface of a plate-like head (51) of a rivet member (54), and a washer member (53), electrical resistance in a mutual contact surface becomes very small.

[0016]In concrete composition of this invention, said two or more collecting terminals are arranged at a position which carries out the abbreviation division-into-equal-parts rate of the length when a spiral axis is developed. Since current collection is uniformly performed by two or more collecting terminals from a rolling-up electrode body according to this concrete composition, high collecting performance is obtained.

[0017]In other concrete composition, a crevice (55) of conical shape reduced toward cylindrical shape or a method of the back is formed in an apical surface of a shank (52) of a rivet member (54) which constitutes each collecting terminals (5). Since thickness of a shank (52) which surrounds said crevice (55) becomes thin according to this concrete composition, in a caulking process, big power is unnecessary.

[0018]As collecting terminals (5) by the side of an anode, and construction material of a lead (7), aluminum, stainless steel, nickel, etc. can be used and copper, stainless steel, nickel, etc. can be used as collecting terminals (5) by the side of a negative electrode, and construction material of a lead (7). As positive active material, at least a kind of material chosen from a group which consists of $LiCoO_2$, $LiNiO_2$, $LiCo_{1-X}nickel_XO_2$, $LiMn_2O_4$, and these conjugated compounds of a metallic oxide can be used.

As construction material of negative electrode active material, conductive polymers, such as metallic-oxide materials, such as carbon materials, such as black lead and corks, a lithium metal, a lithium alloy, $Li_XFe_2O_3$, and Li_XWO_2, and polyacethylene, are mentioned. As an electrolyte, $LiPF_6$ containing metal ions, such as a lithium ion, $LiClO_4$, $LiCF_3SO_3$, etc. are mentioned. It is independent to an electrolytic organic solvent, or ethylene carbonate, diethyl carbonate, dimethoxymethane, sulfolane, etc. can be mixed and used for it. As an electrolysis solution, a solution which dissolved said electrolyte in these solvents at a rate of 0.7 - 1.5M (mol/l) grade is mentioned.

[0019]

[Effect of the Invention]Since the work which attaches collecting terminals (5) to the axis non-coating part (40) of a rolling-up electrode body (4) is simple according to the cylindrical nonaqueous electrolyte secondary battery concerning this invention, productivity higher than before is realized. Since the electrical resistance between a rolling-up electrode body (4) and an electrode terminal part can be suppressed small, collecting efficiency is improved and power density higher than before is obtained.

[0020]

[Embodiment of the Invention]Hereafter, this invention is concretely explained over a drawing about the gestalt carried out to the cylindrical rechargeable lithium-ion battery.

[0021]As shown in drawing 4 and drawing 1, inside the cylindrical battery can (1) which carries out welding immobilization of the lid (12) and (12), the cylindrical rechargeable lithium-ion battery of example this example accommodates a rolling-up electrode body (4) in the both ends of a barrel (11),

and is constituted to them.The electrode terminal mechanism (9) and (9) of the positive/negative couple is attached to both the lids (12) and (12), It is possible for it to be mutually connected by the collecting structure which the two poles and the two-electrodes terminal mechanism (9) and (9) of a rolling-up electrode body (4) mention later, respectively, and to take out outside the electric power which a rolling-up electrode body (4) generates from the electrode terminal mechanism (9) of a couple and (9). The gas exhaust valve (13) of the pressure sliding type is attached to each lid (12).

[0022]As shown in drawing 7, a rolling-up electrode body (4) makes a band-like separator (42) intervene between a band-like anode (41) and negative electrode (43), respectively, winds these spirally and is constituted. An anode (41) applies the positive active material (44) which consists of a lithium multiple oxide to both sides of the band-like axis (45) which consists of aluminium foil, and is constituted, and a negative electrode (43) applies the negative electrode active material (46) containing a carbon material to both sides of the band-like axis (47) which consists of copper foil, and is constituted. Nonaqueous electrolyte is impregnated with the separator (42). The axis non-coating part (40) by which positive active material (44) is not applied to one end of an anode (41) is formed, and the axis non-coating part (40) to which negative electrode active material (46) is not applied is formed in the end of another side of a negative electrode (43).

[0023]In production of a rolling-up electrode body (4), respectively an anode (41) and a negative electrode (43) are shifted crosswise, are piled up on a separator (42), and are rolled round spirally. By this, at one end, among the both ends of the volume shaft orientations of a rolling-up electrode body (4). The edge (48) of the axis non-coating part (40) of an anode (41) projects to the method of outside [edge / of a separator (42)], and the edge (48) of the axis non-coating part (40) of a negative electrode (43) has projected to the method of outside [edge / of a separator (42)] in the end of another side.

[0024]And two or more collecting terminals (5) are attached to the both ends by the side of the anode of a rolling-up electrode body (4), and a negative electrode, respectively. Collecting terminals (5) comprise a rivet member (54) and a washer member (53), as shown in drawing 3 (a). The rivet member (54) protrudes the plate-like head (51) on the base end of a shank (52), and the cylindrical crevice (55) is formed in the apical surface of a shank (52). It is also possible to change to a cylindrical crevice (55) and to form the crevice (55) of the conical shape reduced toward the method of the back as shown in the figure (b). The collecting terminals for anodes (5) are the products made from aluminum, and the collecting terminals for negative electrodes (5) are copper.

[0025]As shown in drawing 1, each axis non-coating part (40) of a rolling-up electrode body (4), Length when an axis is developed is divided into the ring shape field (4a) (4b) (4c) which is three which becomes equal, collecting terminals (5) are attached to each ring shape field so that a ring shape field may be put from both sides, and six non-coating axis bunches (49) are formed in it of this. And the base end of the band-like lead (7) is connected with each collecting terminals (5), and the lead (7) which is the six sheets with same polarity is connected with the flange (92) of one electrode terminal mechanism (9).

[0026]Drawing 2 (a), (b), and (c) expresses the process of attaching collecting terminals (5) to the axis non-coating part (40) of a rolling-up electrode body (4). As first shown in the figure (a), where a lead (7) and an axis non-coating part (40) are inserted between a rivet member (54) and a washer member (53), The shank (52) of a rivet member (54) is made to penetrate to the breakthrough (56) of a lead (7), an axis non-coating part (40), and a washer member (53), as shown in the figure (b). To the lead (7) and the axis non-coating part (40), the hole for making a shank (52) penetrate is established beforehand.

[0027]Then, like drawing 2 (c), where a lead (7) and an axis non-coating part (40) are strongly compressed by the plate-like head (51) and a washer member (53), the tip part (52a) of a shank (52) is closed. As a result, a non-coating axis bunch (49) is formed, a non-coating axis bunch (49) is strongly compressed by the plate-like head (51) and washer member (53) of a rivet member (54) from both sides, and axis sides stick it by pressure strongly by them. Here, since the shank (52) of a rivet member (54) has penetrated the non-coating axis bunch (49) and the lead (7), even if big pull strength acts on collecting terminals (5), a possibility of separating from a non-coating axis bunch (49) and a lead (7) does not have a rivet member (54).

[0028]As shown in drawing 1, an electrode terminal mechanism (9) is provided with the electrode terminal (91) attached by penetrating the lid (12) of a battery can (1), and the flange (92) is formed in the base end of this electrode terminal (91). The breakthrough of a lid (12) is equipped with an insulating member (93), and the electrical insulation and sealing nature between a lid (12) and an electrode terminal (91) are maintained. A washer (94) is inserted in from the outside of a lid (12), and the 1st nut (95) and the 2nd nut (96) are screwing in an electrode terminal (91). And sealing nature is improved by binding the 1st nut (95) tight and compressing an insulating member (93) with the flange (92) and washer (94) of an electrode terminal (91). The tip part of the lead (7) extended from each collecting terminals (5) is welded to the rear face of the flange (92) of an electrode terminal (91). The lead (7) by the side of an anode is a product made from aluminum, and the lead (7) by the side of a negative electrode is copper.

[0029]In the above-mentioned cylindrical rechargeable lithium-ion battery, since collecting terminals (5) are attached to each non-coating axis bunch (49) of a rolling-up electrode body (4) by caulking immobilization, they do not need to perform welding etc. and are as simple as a fitter. A non-coating axis bunch (49) is strongly compressed by the plate-like head (51) and washer member (53) of a rivet member (54) from both sides, and axis sides stick it by pressure strongly. Here, since the shank (52) of a rivet member (54) has penetrated the non-coating axis bunch (49) and the lead (7), even if big pull strength acts on collecting terminals (5), a possibility of separating from a non-coating axis bunch (49) and a lead (7) does not have a rivet member (54). Thus, the axis sides of a non-coating axis bunch (49) are stuck by pressure strongly mutually, and a non-coating axis bunch (49) and a lead (7), Since it is strongly stuck by pressure with the inner surface of the plate-like head (51) of a rivet member (54), and a washer member (53), the electrical resistance in a mutual contact surface becomes very small. Since the thickness of the portion which surrounds the crevice (55) of a shank (52) becomes thin, in a caulking process, big power is unnecessary. With two or more collecting terminals (5), since current collection is uniformly performed from a rolling-up electrode body (4), high collecting performance is obtained.

[0030]Next, the manufacturing method of the cylindrical rechargeable lithium-ion battery of this example is explained.

[0031][Production of an anode] Carbon as $LiNi_{0.7}Co_{0.3}O_2$ and the conducting agent as positive active material is mixed at a rate of the weight ratio 90:5, and positive electrode mixture is obtained. Next, the polyvinylidene fluoride which is a binder is dissolved in N-methyl-2-pyrrolidone (NMP), and a NMP solution is prepared. And positive electrode mixture and a NMP solution are kneaded so that the weight ratio of positive electrode mixture and polyvinylidene fluoride may be set to 95:5, and a slurry is prepared. This slurry is applied to 20-micrometer-thick both sides of the aluminium foil as an anode axis with a doctor blade method, vacuum drying of 2 hours is performed at 150 **, and an anode is obtained.

The non-coating part whose width from the axis edge is 20 mm is formed in an anode axis.

[0032][Production of a negative electrode] The polyvinylidene fluoride which is a binder is dissolved in NMP, and a NMP solution is prepared. And graphite powder, corks powder, and a NMP solution are kneaded so that the weight ratio of graphite powder, corks powder, and polyvinylidene fluoride may be set to 72:18:10, and a slurry is prepared. This slurry is applied to 10-micrometer-thick both sides of copper foil as a negative-electrode axis with a doctor blade method, vacuum drying of 2 hours is performed at 150 **, and a negative electrode is obtained. The non-coating part whose width from the axis edge is 20 mm is formed in a negative-electrode axis.

[0033][Adjustment of an electrolysis solution] $LiPF_6$ is dissolved in the solvent which mixed ethylene carbonate and diethyl carbonate by the volume ratio 1:1 at a rate of 1 mol/L, and an electrolysis solution is adjusted.

[0034][Assembly of a cell] The rolling-up electrode body (4) shown in drawing 7 is produced using the anode and negative electrode which were obtained by the above process, and the separator which consists of fine porous membrane made from polyethylene of ionic permeability. and length as shown in drawing 1, when the axis of each positive and negative poles is developed -- abbreviation -- an axis non-coating part (40) is divided into three ring shape fields (4a) (4b) (4c) so that it may become equal. Next, as shown in drawing 2 (a) and (b), a breakthrough is established to each lead (7) and an axis non-coating part (40), the shank (52) of a pin member (54) is inserted in this breakthrough, and a washer member (53) is inserted in at the tip of this shank (52). And as shown in the figure (c), where a non-coating axis bunch (49) and a lead (7) are compressed, the tip part (52a) of a shank (52) is closed. Then, a rolling-up electrode body (4) is accommodated in a barrel (11). On the other hand, an electrode terminal mechanism (9) is attached to each lid (12), and the tip part of the lead (7) extended from each collecting terminals (5) by the side of an anode and a negative electrode is welded to the rear face of the flange (92) of the electrode terminal (91) by the side of an anode and a negative electrode, respectively. Finally, welding immobilization of the lid (12) is carried out at each opening of a barrel (11), and the cylindrical rechargeable lithium-ion battery of this example is assembled.

[0035]The conventional cylindrical rechargeable lithium-ion battery (conventional cell) which has the collecting structure shown in the cylindrical rechargeable lithium-ion battery (example cell) shown in measurement drawing 1 of internal resistance and drawing 5 was produced, and alternating current impedance was measured as internal resistance of each cell.

[0036][Production of the conventional cell] By the making process of the anode and the negative electrode, the anode and the negative electrode were produced like the above-mentioned example except having applied the slurry to the axis completely, without providing an axis non-coating part. In the assembly of a cell, as shown in drawing 6, 15 electrode tabs made from aluminum were welded to the surface of the aluminium foil which constitutes the anode at intervals of 20 cm, and 15 copper electrode tabs were welded to the surface of the copper foil which constitutes the negative electrode at intervals of 20 cm. And the separator which consists of fine porous membrane made from polyethylene of ionic permeability was inserted between the anode and the negative electrode, and winding and a rolling-up electrode body (2) were spirally produced for these. The thickness of the electrode tab of an anode and a negative electrode was 0.1 mm. And as shown in drawing 5, the electrode tab (3) of each electrode was welded to the flange (92) of the electrode terminal mechanism (9), and the cell was assembled conventionally. The active material coverage of each electrode of a cell used an equivalent amount

conventionally with the example cell, and the size of each cell presupposed that it is the same.

[0037][Measuring method] Before accommodating the rolling-up electrode body of each cell in a barrel, the alternating current impedance at 1 kHz was measured. The anode and negative-electrode side performed measurement between the axis non-coating part and electrode terminal which are located in the outermost periphery part of a rolling-up electrode body.

[0038][Measurement result] The result shown in the following table 1 was obtained about the cell an example cell and conventionally.

[0039]

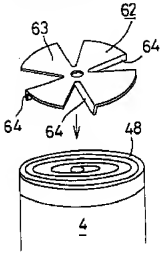
[Table 1]

電　池	負極側インピーダンス	正極側インピーダンス
実施例電池	３．８ｍΩ	８．０ｍΩ
従来電池	１０．８ｍΩ	２５．５ｍΩ

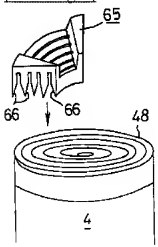
[0040]Also in any by the side of an anode and a negative electrode, so that clearly from the result shown in Table 1 the alternating current impedance of an example cell, It is conventionally smaller than the alternating current impedance of a cell, and according to the cylindrical rechargeable lithium-ion battery of this invention, it can be said from this that power density higher than the conventional cell can be obtained.

DRAWINGS

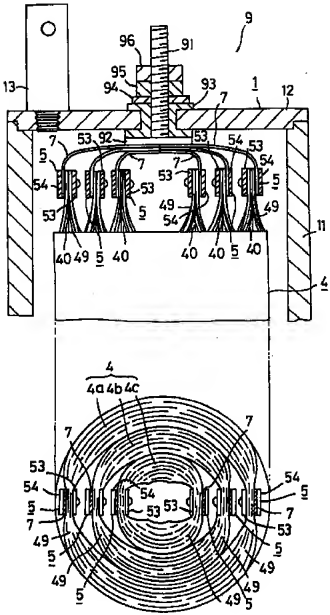
[Drawing 8]



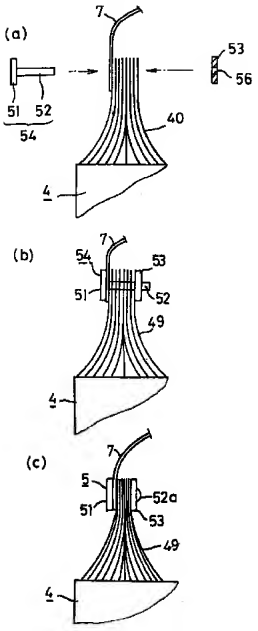
[Drawing 9]



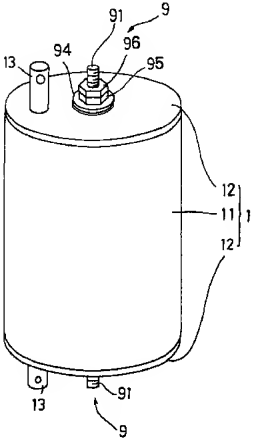
[Drawing 1]



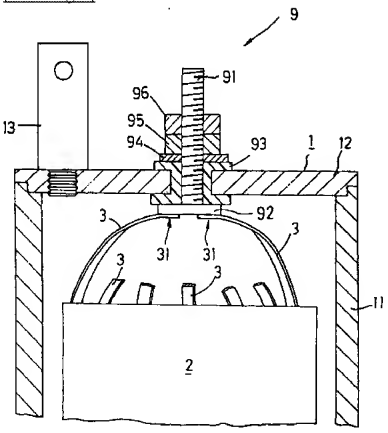
[Drawing 2]



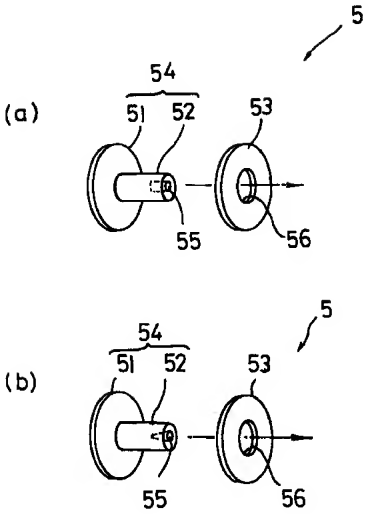
[Drawing 4]



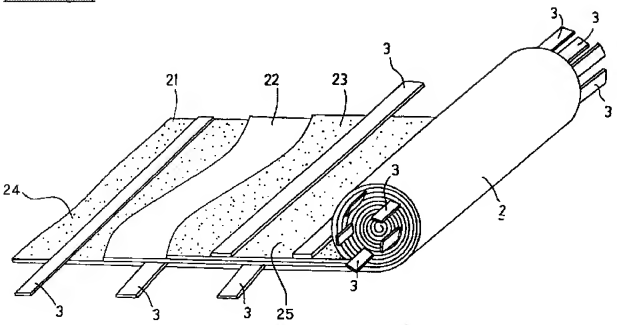
[Drawing 5]



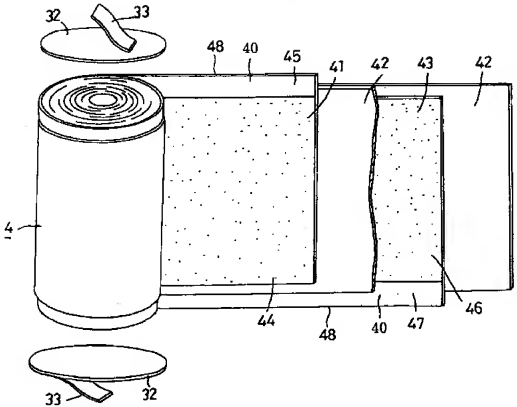
[Drawing 3]



[Drawing 6]



[Drawing 7]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